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STUDIES ON THE DURABILITY OF POLYMER MATERIALS

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16. Abstract

In order to establish a comprehensive evaluation system for the durability of polymer materials, this research project has been started in 1972 fiscal year with the cooperation of eight institutes affiliated with the Agency of Industrial Science and Technology, and continued seven years. Six Polymers, i.e., polystyrene, polyvinyl chloride, polymethyl methacrylate, polyoxymethylene, polyacrylonitrile-butadiene-styrene and polyethylene were chosen for this purpose. The testing conditions include application of mechanical force, storage at various room temperature, weathering in four different regions (up to five years), exposure to seven artificial lights and exposure to heat and chemicals. Tests are made on (1) physical properties, i.e., tensile and bending characteristics, impact strength, fatigue, creep, etc., (2) structural factors, i.e., erosion, molecular weight, infrared absorption, etc., and (3) apparent features, i.e., dimension, shape, weight, luster, color, surface smoothness, etc.

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STUDIES ON THE DURABILITY OF POLYMER MATERIALS

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1. OUTLINE OF RESEARCH

Polymer materials, nowadays, are the chief materials indispensable for human life and industry. They are widely used at various atmospheric conditions, and durability of polymer materials is an important problem. Until present, there are no study for a comprehensive evaluation of the durability of polymer materials. Such study requires a long time and many researchers of the special field which covers a wide range.

In order to establish a comprehensive evaluation system for the durability of polymer materials, this research project has been started in 1972 fiscal year with the cooperation of eight institutes affiliated with the Agency of Industrial Science and Technology, and continued seven years. Six Polymers, i.e., polystyrene, polyvinyl chloride, polymethyl methacrylate, polyoxymethylene, polyacrylonitrile-butadiene-styrene and polyethylene were chosen for this purpose. The testing conditions include applicatic of mechanical force, storage at various room temperature, weathering in four different regions (up to five years), exposure to seven artificial lights and exposure to heat and chemicals. Tests are made on (1) physical properties, i.e., tensile and bending characteristics, impact strength, fatigue, creep,

etc., (2) structural factors, i.e., erosion, molecular weight, infrared absorption, etc., and (3) apparent features, i.e., dimension, shape, weight, luster, color, surface smoothness, etc.

1. Objective of the Research

The polymer materials are widely used in many fields, such as electricity, mechanics, vehicles, architecture, engineering works, agriculture, and fishery, as well as familiar plastic household utensils. They are now one of most important materials indispensable to national life and industry. On the other hand, the polymer materials have been rapidly developed in a short period of time about 30 years. Therefore, the history as a material is short and the experiential credibility and technical information regarding their durability have not been sufficiently accumulated yet.

Nowadays, in the age of natural resource and energy conservation, it is a very important subject for the industry and national life to improve the durability of polymer materials, whose main source is petroleum, and to consolidate the credibility of their durability, in the aspects of natural resource conservation, energy conservation, consumer protection, and security confirmation.

Durability is a chronological character preservation of an object under circumstantial condition, such as natural, environmental conditions, and under thermal, mechanical, and chemical conditions in use. It is a total

quality associated with the durable life of a material or a product.

So far, many studies have been done regarding the durability of polymer materials. However, they all investigated the degradation mechanism at a molecular level, or the degradation pattern of characteristics of an object, about one or two affecting factors which were supposed to be the degradation factors from their point of view. They only obtained segmental findings. Therefore, there is almost no report in which the durability /1* was comprehensively evaluated and the information for the establishment of the optimum planning standards has not been sufficiently accumulated yet.

On the other hand, as for the evaluation method of durability of polymer materials, because the causality of durability is diverse and complicated, no standard method with high credibility has been established. However, in order to evaluate durability comprehensively, a long period of studies by the researchers of a wide range of specialty is required and this kind of study is an important subject for the nation but is not directly related to corporate profits. Therefore, the execution of a generalized study by a national research institute needed.

Responding the needs above, this research project was executed as a joint research by eight institutes affiliated with the Agency of Industrial Science and Technology (AIST) and its objective is to evaluate the durabil-

* Numbers in the margin indicate pagination in the foreign text.

ity of polymer materials comprehensively as well as to obtain the information for the production of the optimum planning standards. For this purpose, the six standard sheet materials, i.e., polystyrene, polyvinyl chloride, polymethacrylate, polyoxymethylene, ABS, and polyethylene were selected as the main subjects, and the versatile research was performed on degradation mechanism, evaluation method, and evaluation of characteristics.

2. Circumstances of the Research

In 1972, when this research started, it was in the high economical development period of our country and the polymer industry based on the petroleum chemistry was in its peak development period. Consequently, the mass-production and mass-consumption associated with the rapid development resulted in so-called "plastics pollution". This brought us the problems what polymer materials should be as the short-term consumption materials.

Under those circumstances, in 1971, in the meeting of the Weather Resistance Section, which is a subdivision of the Polymer Researchers' Liaison Conference in the Agency of Industrial Science and Technology, the necessity of a joint research on the weather resistance of the polymer materials was proposed. Moreover, it was adopted in the Conference as a whole and the participating researchers were rallied through the organization. As a result of the further discussion on the contents and plans of the research, the objective bounds of the research was extended to the

durability of polymer materials and the execution of a comprehensive joint research was planned. Following the basic plan, the persons in charge of polymer in the Business Department of AIST, the planning members of the Conference, and the representatives of each research institute, examined and summarized the specific research contents proposed from each participating testing institute, and proposed a research plan of "Studies on the durability of Polymer Materials" as a 5-year special research beginning 1972. Its execution was assessed and the research was initiated in 1972.

The Polymer Researchers' Liaison Conference of AIST, which was the mother organization of this joint research, is a voluntary organization of interested researchers started in 1966 as a place for polymer researchers in the research institutes affiliated with AIST to exchange their information, present and discuss their studies. This Conference had developed and was reorganized as an official research promotional organization of AIST and its name was changed into General Promotional Conference for Polymer Research in 1975.

This research can be said to be the outstanding research because this project was evolved by the meetings of those researchers responding to needs of the age and also because it was executed by many institutes with different specialties.

Regarding the promotion and management of the research, the information exchange between the projects, discussion and adjustment of a

project were carried out under the organization and structure shown in the appendix. Moreover, the Comprehensive Evaluation Committee was established in AIST in 1978 and the integration of the research results has been done.

The research was originally started in 1972 as a 5-year project. However, since a lot of time had been consumed in the selection of the standard common samples, molding, adjustment of test pieces, preparation for experiments, and preliminary examination, and the initiation of the real experiments had been delayed, the period of some part of the research, such as weather resistance, dimension, shape, and standard data of the preserved samples, which required 5 years for the experiments, were extended for 2 more years. During that period, some short term supplemental experiments were performed. Finally, all the special research had been finished in 1978. The most of the research was executed as special research but some of them was executed as an ordinary research of each institute.

The individual fruits obtained in the course of the research have been reported in the conferences, society meetings, lectures and journals one after another as listed in the appendix at the end. Also, the interim comprehensive reports were carried out in the 13th Polymer Research Meeting held at Gakushi Kaikan in October, 1977, and in the 15th Polymer Research Meeting held at Sanseido Building in November, 1979.

Nowadays, in the natural resource and energy conservation age, 8

years after the initiation of the research, the meaning of this research is so important that it can not be compared with that when the research started before the oil shock. The fruit of this unique comprehensive research, which systematically analyzed and evaluated the durability of polymer materials, not only supplies the important fundamental data for the development and material planning of durable polymers but also has various influence and effects including revision of present JIS and proposal of new standards, and establishment of the comprehensive evaluation system of durability.

3. The Summary of Contents and Results of the Research

Utilizing the six kinds of common sheet samples of polystyrene (PS), polyvinyl chloride (PVC), polymethyl methacrylate (PMMA), acrylonitrile-butadiene-styrene (ABS), polyoxymethylene (POM), and polyethylene (PE) as the main subjects, regarding the various outer mechanical, atmospheric, /2 thermal, and chemical conditions, the durability was analyzed and evaluated in the aspects of various mechanical properties, structural factors, morphological properties, and thermal properties. Table 1 shows the contents of the research in combination of outer conditions and evaluation property items. The symbols denote the institute executed.

In 2 or 3 TG researches, such as fatigue, and heat degradation, depending upon the necessity of the research, beside the 6 kinds of common samples, the samples of each TG's own were added and the experiment was

TABLE 1-1 CONTENTS OF THE RESEARCH AND THE ORGANIZATIONS EXECUTED

Outer Conditions		Evaluation Items	Mechanical Properties									
			Tensile	Bending	Compression	Shearing	Impact	Hardness	Abrasion	Fatigue	Creep	Visco-elasticity
Mechanical	Fatigue	Repeated Deformity								M P H S O Ku 1	O 2	
	Creep	Constant Load										
	Abrasion	Friction							M O 2'			
Atmospheric	Preserved Samples	Constant Temp. -20, 0, 20, 40°C	O H* 3	O H* 4	O 5		O H* 6	H* 7	O* 8		O* 9	
	Weather Resistance	Open Air Exposure 4 Locations	H 16	H 17			H 18	H 19	M* 20	H* 21	P* 22	P* 23
	Weather Resistance	Accelerated Exposure 7 Models	H 34	H 35			H 36'	H 37				P* 28
		Non-exposure 63°C	H 44	H 45								
Thermal	Thermal Degradation	High Temp. Higher than 60°C	S 46	S 47								
	Low Temp. Properties	Low Temp. Lower Than Room Temp.	R 49	R 50		R 51						
Chemical	Water Resistance	Water Hot Water	P* 52									
	Chemical Resistance	Organic Solvent	P* 53									
Original Data (see other table)			O	O	O		O	O	O	O	O	

*: Executed a part of a project

K: Keiryoken M: Kigiken T: Kagiken O: Daikoushi P: Senkouken S: Seikeken R: Koushiken H: Hokukeishi Ku: Kyukoushi

TABLE 1-2 CONTENTS OF THE RESEARCH AND THE ORGANIZATIONS EXECUTED

Structural Factors			Morphological Properties							Thermal Properties			
Molecular Weight	Infrared Spectrum	Corrosion Process	Density	Weight	Dimension	Shape	Luster	Roughness	Discoloration	Softening Point	Linear Expansion	Heat Conductivity	Transposition Temperature
T* O* 10			K* 11		K* 12		H* 13		H* O* 14				
T* H* O 24	S 25	P* 26		P* 27	P* K* 28	K* H* 30	H P 31	K* 31'	H O* P 32				
T* H* O 24		P* 39			K* H 40	H* 41	H P 42		H O* P 43				
H* 24													
T* O* 24					K* 48								
O			O						O	O	O	O	O

Note for Table 1

2 Tensile creep, creep rupture

2' M, O testing methods

3 O: yielding strength, fracture strength, fracture extension

H: 20°C, at fifth year

4 O: strength, elasticity

H: 20°C, at fifth year

5 Strength

6 O: Charpy, Izod

H: 20°C, at fifth year, Charpy (tensile fracture energy)

7 20°C, at fifth year

8 20°C, Tayber, ASTM

9 20°C, each 1.5 years, 100 hours, tensile creep

10 T: PS, PMMA, PVC, fifth year

O: PE, third year

11, 12 20°C and general room preservation, 5 years

13 20°C, preserved samples

14 H: 20°C, preserved samples

O: room preservation samples, third year

18 Fracture energy

19 Barcoal hardness

20 Exposure site H, friction properties of 1, 2, and 3 years

21 Exposure site H, 1-3 years, 5 kinds except for PE

22 Exposure site W, PS, PMMA, PE, 20°C bending creep

23 Exposure site W

Note for Table 1 (continued)

24	T: PS, PMMA, PVC
	O: PE
	H: PE
26	Exposure site W
27	Exposure site P
28	P: Exposure site P
	K: Exposure site W
30	K: Exposure site W
	H: Surface observation
31'	Exposure site W
33	Final exposure samples, exposure site W
36	Fracture energy
37	Barcol hardness
40	K: Ultraviolet carbon arc type
	H: Sunshine weather type
41	Weather accelerated exposure surface observation
44, 45	Preserved samples at black panel temperature
46	Elasticity, fracture
48	Temperature cycle 80°C↔-30°C, 60°C↔-10°C

(Exposure site W is the symbol for Japan Weathering Test Center Choshi Exposure site)

performed on them.

Also, in the research of weather resistance, in order to obtain reference data to the sheet common samples, an original research utilizing the film samples and colored plastic samples as described below was performed.

3.1 Durability Against the Mechanical Force

3.1.1 Fatigue

(1) Fatigue Properties

Besides 6 common samples, 9 kinds of samples, of which fatigue is an important feature, were added. Total 16 samples were used. The standard S-N curve in the atmosphere of 20±2°C, and 65±5%RH was obtained from the testing machines in 6 institutes including different models. The difference between models was also assessed. Moreover, at 2 institutes, 6 levels of temperature dependence at -20°C - +60°C were investigated, and the rise of test piece surface temperature during the fatigue test, and the decrease in rigidity were also assessed. As a result, the reliable data of a wide range of materials were obtained and the fatigue properties became more definite. At the same time, however, the fact there is a large bias between the testing machines was made clear. The reason for that is unknown in most cases, but in some cases, it was found to be due to the difference or

deviation in adjustment of testing machines. Based on the results, when JIS, K7118, and 7119 regarding the fatigue test of hard plastic materials would be revised, it was proposed that checking the zero load point and the resonance point (maximum load amplitude point) of the testing machines (no-equilibrium weight rotation type) be performed before the initiation of the test. Also, as a result of the assessment of temperature dependance, the fatigue destruction can be classified into three types and it was found that even the same sample changed its destruction type depending upon the atmospheric conditions. Furthermore, the rise in surface temperature and change in rigidity during the test were also clarified.

(2) Fatigue Properties of the Plastics Exposed to the Open Air

The polymer materials have been increasingly used in the condition under a varying load in the open air. It is important as a planning data to clarify the association of the durability, static and dynamic strength of the polymer materials in those cases. However, there is hardly any report describing the fatigue properties under those conditions. In this research, utilizing 5 kinds of thermoplastic resins (PS, PVC, PMMA, ABS, POM) among the common samples of the joint research and additional 3 kinds of FRP (UP-CSM, UP-PWC, UP-(WR+CSM)) as subjects, the open air exposure examination was performed for maximum 3 years. The tensile strength, bending strength, and fatigue strength after the exposure were measured and the chronological change and its correlations were assessed. As a result, it was found that resins with extreme surface degradation due to the

exposure, such as PS, ABS, and POM among the thermoplastic resins, show a larger reduction rate of fatigue strength than that of static strength. Therefore, they require special care in material planning. On the other hand, PMMA and PVC, whose surface changes are minimal, the reduction rates of fatigue strength almost correlate to those of static strength. Contrary to them, FRP demonstrated the surface change due to the exposure, such as yellowing and looming of glass fibers, but the static strength of three kinds was not reduced while the fatigue strength of UP-(WR+CSM) decreased about 15%. Thus, they are strongly weather resistant. The important information in the material planning as described above was obtained.

3.1.2 Creep

(1) Tensile Creep Properties

Using the 6 kinds of common samples, the chronological research regarding the creep fracture curves of the original samples, and the creep strain curves of the materials preserved in the standard atmosphere (20±1°C, 65±5%R.H.) for 3 years at 1.5 year intervals has been performed. Also, the creep strain curves were plotted on the Gonbertz curve and their coefficients were compared so that the variation among the creep strain curves of the polymer materials was assessed.

As a result, the followings were found: a) The creep fracture strength

at 100 hours (in PCM and PE, the creep strength at 100 hours when the creep strain becomes 10%) is approximately 35-70% of the tensile strength. b) Utilizing the statistical method, the significance of the difference among the creep strain curves was evaluated. As a result, the significance was recognized but, considering the dispersion, it can not say that there is a characteristic tendency in the difference among the creep strain curves.

(2) Bending Creep Under Exposure

A device which can expose the samples under a loaded condition was produced for trial. It was established in the Japan Weathering Test Center in Choshi in August, 1974, and the experiment was started. Three levels of load were laden to each of the 6 kinds of the common samples and their amount of bending pliability had been measured for a long period of time. The change of the bending pliability, correlation between the fracture time and the load, and the relation between the fracture time and the bending pliability at the time of fracture, were evaluated.

The bending pliability under exposure is affected by the temperature of a year. In July and August, when the temperatures are high, the creep amount increases but it does not in the low temperature season. Because of the repetition of it, the amount of the bending pliability gradually increases and finally fractures occur. Despite the loaded weight was considerably lighter than the strength in the standard condition, the fractures occurred under the exposure. As a result of the evaluation of the relation between

the fracture time and the amount of pliability at the time of the fracture among the samples fractured, the difference between the resins easily affected by the exposure and the resins resistant to the exposure was clarified. According to the result of the research, PE, PS, PMMA, and PVC are greatly affected by the exposure, in this order. [14]

3.1.3 Abrasion

(1) Abrasion Properties

Using the Tayber type abrader, the effect of the various factors affecting the abrasion loss of the polymer materials, such as the rotation speed of the sample, the test load, kinds of abrasion ring (so-called "whetstone"), the structure of the mounting axis of the abrasion ring, and the structure of the abrasion ring mounting arm, has not been clarified systematically. The effects of those factors were assessed in this research.

The Tayber type abrasion test and ASTM-A type abrasion test were performed to the common samples stored at a room temperature of 20°C and 65%R.H. of humidity, and the chronological change of the coarse abrasion loss for 5 years was investigated. The Tayber type abrasion loss increased in the first year. However, it decreased gradually after the first year. The ASTM-A type abrasion loss did not show any chronological change when the test results were organized in the JIS method. However, when the results were reorganized on the basis of the measured layers of the

samples, such as surface layers, and deep layers, it was found that there are some materials which show a chronological change.

Also, it is common that the abrasion test results vary a lot depending upon the abrasion test machines. Moreover, in most cases, the cause is unknown. This disturbs the accurate evaluation. In this research, regarding the ASTM-A type abrasion test machines, the effects of the size of the test pieces to abrasion associated with the "uneven contact (kataatari)" of the test pieces were investigated. As a result, contrary to the orthodox idea that the abrasion does not depend upon the size of the test pieces, it was found that the degree of abrasion strongly depend upon the area of a test piece in contact with the machine and therefore, a "warp", "winding" or unevenness of the opposing surface due to the abrasion affect significantly. Also, it was found that the use of a free handle to reduce the "uneven contact" unexpectedly increases the "uneven contact" and promotes the disperse. Those points contribute as the data for the establishment of the standard (JIS 7205) of the abrasion test method and its revision.

(2) The Change of the Abrasion Properties Caused by the Open Air Exposure

In order to clarify the the change of the abrasion properties caused by the open air exposure, the common samples exposed to the open air for 5 years at 4 locations (Hokkaido, Choshi, Yokohama, and Okinawa) underwent the ASTM-A type coarseness abrasion test. Because the degradation was considered to be more progressive near the surface, the abrasion loss was

measured after each 250 rotations instead of each 1000 rotations, which is standardized in JIS. As a result, the progression of the degradation in each exposed location varies a little depending upon the material. In all cases, the materials in Okinawa demonstrated the most severe degradation and the next was Yokohama. Those data clarified the abrasion properties in a long-term use and are very valuable in terms of the practical characteristics.

(3) The Change of the Friction Coefficient Caused by the Open Air Exposure

Although the change of the friction coefficient when a plastic material have been exposed to the open air for a long period of time is an important question in practice and the academic studies, the data regarding this can hardly be found. In this research, the correlation between the friction coefficient and exposed period was investigated to the 6 common samples using a rigid ball as a partner.

As a result, every resin's friction coefficient increased after the open air exposure. Especially, ABS and polystyrene showed 30-50% increase in friction coefficient after 1 year of exposure.

3.2 Durability in the Atmospheric Air

3.2.1 Samples Stored in a Room

(1) Static Dynamic Properties

The chronological change of tensile strength at a year interval as well as compression and bending of the common samples stored at a room temperature (20°C, 65%R.H.) was measured. The objective was to clarify the characteristics and the degree of the chronological change of each sample. Also, in order to investigate the influence of thermal factors on strength in details, the test materials were stored in the 4 levels of thermal atmosphere within a range of -20 - +40°C and the measurement was performed to them.

As a result, when stored in a room, the tensile yield strength of PVC increased, as already known. However, it was found that the compression yield strength and bending yield strength also increases. On the other hand, the yield strength of PMMA, PS, POM, ABS, and PE other than PVC demonstrated almost no chronological change. When stored in the thermal atmosphere near the room temperature, in case of PVC, POM, ABS, and PE, the strength tends to gradually increase as the atmospheric temperature rises. But PMMA and PS showed no change of strength. Those results are useful findings in the dynamic property testing method as the data for selection of the reference material used to confirm that the test conditions are appropriate.

(2) Impact Properties

In order to investigate the 5 year chronological change of the impact

properties of the 6 common samples preserved in the thermostats of 40°C, 20°C, 0°C, and -20°C avoiding the light, two kinds of Charpy impact values (No. 1 and No.2 test pieces) and Izod impact values were measured. As a result, the following was found. a) No characteristic change in appearance was found in the samples preserved for 5 years. b) In general, each sample's impact value tends to decrease as time passes. However, some samples preserved in a lower temperature showed an increase for unknown reason. c) The impact values simply neither increased nor decreased /5 chronologically. Some of impact values showed very complicated course of change. This phenomenon was observed in some materials which showed brittle fractures. d) Three kinds of test pieces of the two samples (ABS, PE) demonstrated a no-fracture condition associated with plastic deformation. All other samples demonstrated a separation fracture which can be considered as a complete brittle fracture. e) Nearly half of the samples showed a distinctive correlation between the time period and the impact values as a result of correlation analysis. f) Sample pieces obtained in a longitudinal direction of a plate have slightly higher impact values than those obtained in a right angle. However, only PE could be identified its direction from the impact values.

(3) Density Change of the Samples Preserved in a Room

The submerged transposition method using distilled water and ethyl alcohol solution (in case of polyethylene only) was employed in order to clarify the conditions of density measurement of polymer materials and

accuracy, and to find the chronological change of the samples when stored in a thermostat or in a ordinary room. The method to measure the polymer's density at a high accuracy was evaluated and approximately ±0.7kg/m^3 of accuracy (95% of reliability) was confirmed to be obtained. This is equivalent to 0.05-0.07% of accuracy rate.

Regarding the stability of density, those of acrylonitrile-butadiene-styrene, polystyrene, and polyvinyl chloride showed almost no variation and polyethylene showed a slight decreasing tendency for 5 years.

(4) Dimensional Change of the Samples Preserved in a Room

The chronological dimensional change of the samples stored in a thermostat or an ordinary room for 5 years was obtained and the dimensional stability of each resin was evaluated. Also, the causative factors of the dimensional change were assessed.

In order to improve the accuracy of measurement of dimension, two basal lines were drawn on each sample by carving method and their distance was measured by a universal measuring microscope.

As a result, when the common samples are stored in a room, either an ordinary room or a thermostat, the dimensional changes of polymethyl methacrylate, polyoxymethylene, and acrylonitrile-butadiene-styrene are large and polyvinyl chloride and polystyrene are stable in dimension. Also,

the dimensional change corresponds to the weight change very well. It was noted that the chronological change of dimension can be separated into the permanent change (contraction), which occurs relatively early, and the periodic seasonal change. The amount of contraction due to the permanent change is approximately 0.05% (50μm of 100mm) at maximum.

Moreover, it was confirmed that the cause of seasonal change of dimension is deeply associated with the humidity condition of the storing circumstances, such as moisture absorption, and dehumidifying.

3.2.2 Open Air Exposure Test

(1) Change of Dynamic Properties and Appearance

The open air exposure tests were conducted to the six common samples at 4 locations (Sapporo, Choshi, Yokohama, and Naha) for maximum 5 years (some are 4 years). Data from Sapporo, Choshi, and Naha were used to evaluate the variation due to the different latitudes. Data from Choshi and Yokohama, which locate at the same latitude, were used to investigate the influence of environmental conditions, such as air pollution.

Regarding the tensile strength, among the dynamic properties, polystyrene, methacrylic resin, ABS resin and polyethylene demonstrated the regional differences in order of the latitudes, in other words, the lower the latitude is, the more severe the degradation is. Vinyl chloride resin and

polyacetal also showed the regional differences due to the latitudes, although, at the end of the exposure, there was almost no difference between them. On the other hand, as for the influence of the air pollution, only vinyl chloride resin and polyethylene showed a significant difference. In both cases, the decrease of the strength was greater in Yokohama, where the air pollution is worse.

Among the appearance changes, as for the fading and discoloration, vinyl chloride resin, methacrylic resin, polyacetal, and polyethylene demonstrated the regional differences due to the latitudes. Similar to the strength, the lower the latitude is, the greater the change is. On the other hand, in polystyrene and ABS resin, of which the minute cracks occur in all directions on the surface, the regional difference was recognized but it was not in order of the latitudes. The change became greater in Choshi, Sapporo, and Naha, in this order. On the other hand, the influence of the air pollution was recognized significantly in vinyl chloride resin, methacrylic resin, ABS resin, and polyacetal. However, three of them, vinyl chloride resin, ABS resin, and polyacetal, showed more severe discoloration in Choshi. It was especially noted that vinyl chloride resin shows a reverse result to the strength. Regarding the luster, among the appearance changes, the regional differences in the order of latitudes were recognized in both vinyl chloride resin and methacrylic resin, which showed minimal changes of the surface condition. Other 4 resins did not demonstrate any significant difference because of the mixture of factors, such as condition of surface cracks, invasion of the polluted materials into the cracks.

(2) Dimensional Change

The common sheet samples had been exposed to the open air for 5 years at Japan Weathering Test Center (Choshi City, Chiba Prefecture) and the dimensional change of the sample had been measured as the change in the distance between two sides, so that the the dimensional stability of each resin was clarified.

After establishing the standard dimension by a bar gauge, the measurement of the distance between two sides was performed using a simple device that measures the deviation by an electric micrometer.

The dimensional change of the common samples exposed to the open air demonstrated a dramatically different tendency from the dimen- /6
sional change when stored in a room. In polyethylene, which showed the largest change, 0.4% of contraction occurred and the significant aeolotropy was recognized. Contrary to it, in methylmethacrylate, which showed the largest contraction in dimension during the storage in a room, approximately 0.1% of expansion was noted. Among six common samples, polyvinyl chloride and polystyrene showed a good dimensional stability. Acrylonitrile butadiene-styrene and polyoxymethylene manifested 0.1-0.2% of contraction. It was confirmed that this contraction, same as that of polyethylene, occurred within the first year after the exposure and there was not a large charge after that.

(3) Molecular Weight and Molecular Weight Distribution

So far, when the durability of polymer materials or degradation was discussed, usually mechanical properties of the materials were adopted as the evaluation method, and the molecular properties of the polymer materials have not been sufficiently discussed. In this research, using GPC method (gel permeation chromatography), the molecular weight and molecular weight distribution of the samples were measured after the various durability tests. As a result, the three kinds of materials except for PVC, in other words, PS, PMMA, and PE, demonstrated a considerable decrease of the molecular weight. Also, their range of the molecular weight distribution tended to be wider. As for PVC, no apparent change was observed and some tests resulted in an increase of molecular weight.

Moreover, as a result of the viscosity measurement, the difference of molecular weight between the surface layer and the inside of the sheet samples was also evaluated.

According to the results, it was found that the measurement of molecular weight and molecular weight distribution by GPC method can be sufficiently and effectively used as the evaluation method of the durability or degradation of polymer materials. Easiness of measuring and that the measurement requires only a few amount of samples are the advantages as the evaluation method.

The viscosity measurement is also widely used in the molecular weight measurement. In this research, it was used together with GPC method and was confirmed to be useful as a evaluation method. However, the molecular weight distribution can not be obtained from the viscosity measurement. When the GPC device can not be used or the sample is not soluble to the solvent of GPC (such as tetrahydrofuran), it would be very useful.

It should be noted that both two methods are relative evaluation methods, not absolute evaluation methods. The absolute measurements of molecular weight (optic scattering, osmotic pressure) are also employed to the unexposed samples. Therefore, those are considered to be available as a standard sample regarding the molecular weight.

The analyzing method of GPC measurement employed in this research, or the viscosity-molecular weight relative expression have a possibility to be a standard method of the measurement of the molecular weight and molecular weight distribution for the samples used in tne research. This will be useful for the evaluation of molecular weight in the polymer industry.

(4) Erosion Process

When light is projected to a polymer material, the degradation occurs.

However, the degree of degradation varies to the thickness of the samples. In a thick sample, the degree of degradation on surface is different from that inside, in association with the strength change and the diffusion of oxygen due to the absorption of optic energy. How much the degradation progressed inside the sample, and how deep the degradation occurred largely affect the characteristics of the material. The condition of erosion due to the degradation was assessed.

The surface of the samples were shaved 0.1 mm, and the amount of yielded carbonyl radicals, which is a basis of the degradation of each layer, and the molecular weight were measured and the degree of degradation inside the sample was evaluated. Also, how the surface degraded layer affects the strength was evaluated by measuring the bending strength of the sample after its surface was shaved.

The surface of the exposed samples were shaved 0.1 mm and the amount of yielded carbonyl radicals and molecular weight of each layer were measured. As a result, it was found that the degree of degradation of surface is different from that inside. The amount of yielded carbonyl radicals decreased as deeper it goes, and in inside, it was almost same as that of unexposed materials.

In a thick material, the inside degradation is minimal. However, it was noted that the surface degradation layer strongly affects the bending strength. Despite the surface degradation layer is thin compared with the

thickness of the total material, it affects inner part where the degradation is minimal. In other words, the degradation layer on surface can be said to have notch effect.

In case of PE, there is a correlation between the amount of yielded carbonyl radicals and Vickers hardness. By measuring Vickers hardness, PE's degree of degradation can be evaluated.

3.2.3 Accelerated Exposure Test

(1) Change of Dynamic Properties and Appearance

At the same time as the open air exposure tests, the accelerated exposure tests using 4 kinds of weathermeters (xenon type, ultraviolet carbon type, sunshine carbon type, and due cycle type), and 3 kinds of fade-o-meters (xenon type, ultraviolet carbon type, and sunshine carbon type) were employed to 6 common samples and the degradation speeds of each resin and each property value were obtained and evaluated. As a result, the test model with a highest degradation speed of each resin and each property value varied and it was found that the previous idea that some specific models have maximum degradation speed in many property values is not always correct.

In short, as for the tensile strength and tensile fracture elongation (the elongation characteristic has a strong correlation with the practical

impact characteristics), among the dynamic properties, the ultraviolet carbon type weathermeter had a maximum degradation speed of polystyrene and polyacetal, the xenon type fade-o-meter had that of vinyl chloride resin, the sunshine carbon type weathermeter had that of methacrylic resin and polyethylene, and the due cycle type weathermeter had that of ABS resin.

On the other hand, as for the fading and discoloration, among the appearance changes, the ultraviolet carbon type fade-o-meter had a maximum degradation speed of polystyrene, the xenon type fade-o-meter had that of vinyl chloride resin and methacrylic resin, the sunshine type weathermeter had that of ABS resin and polyethylene and the due cycle type weathermeter had that of polyacetal. Furthermore, as for the methacrylic resin, the acceleration of the due cycle type weathermeter was the highest and it demonstrates a degradation property which has no similarity to the open air exposure.

Also, as for the luster, a completely different tendency from that of discoloration and fading was indicated and the due cycle weathermeter or the sunshine carbon type had the maximum degradation speed of most of the resins regarding the luster.

Summarizing the changes of strength, fading and discoloration, and luster, the model with a maximum degradation speed of each property value varies and a correspondence is observed only at the strength and fading and

discoloration of polyethylene, and the fading and discoloration and luster of ABS resin. From above findings, by selecting a model which shows the maximum degradation speed from the data for each resin and each property, and by conducting the test with that, it became clear that the test results can be obtained in a much shorter period of time than the current method, regarding the weather resistance. The important findings, in terms of confirmation of the test method as well as the natural resource conservation and the energy conservation, are obtained.

(2) Dimensional Change Due to the Accelerated Tests

In order to promote the dimensional stability of polymer materials exposed to the open air or stored in a room, the tests simulating various environmental conditions were performed and the simple and effective accelerated test method is established. The environmental conditions for test chosen include: a dry atmosphere, a humid atmosphere, a temperature cycle test, ultraviolet irradiation.

In all test environments the experiments were performed, the permanent change (contraction) occurred in the early phase and the change after that was extremely minimal. From this experiment, the primary delay type response was recognized.

The permanent dimensional change during various acceleration tests was large in case of acrylonitrile-butadiene-styrene, polyoxymethylene,

and polyvinyl methacrylate. In case of polystyrene and polyvinyl chloride, it was relatively stable. Polymethyl methacrylate and polyoxymethylene tend to cause the permanent change in response to the humidity change. Also, it was found that polyethylene and polyvinyl chloride are changeable by the temperature cycle.

(3) Change of Luster Due to the Open Air Exposure and Exposure to Accelerated Tester

The sheet common samples were exposed to the open air for minimum 1 year to maximum 5 years at 4 locations and to the 6 models of accelerated testers for minimum 500 hours to maximum 2000 hours. The changes of luster of the exposed samples were measured and the correlations by materials, by exposure locations, and between the open air exposure and accelerated exposure, were evaluated. On the other hand, in order to evaluate the luster changes in the initial phase of exposure, the 10-level open air exposure for minimum 15 days to maximum 14 months and the 9-level sunshine fade-o-meter exposure for minimum 100 hours to maximum 1200 hours were carried out. The measurement was done to each level and, repeating the exposure, the chronological change of luster in the initial phase was obtained.

The chronological change of luster depends upon the materials. Some demonstrate linear change in total course of exposure but some demonstrate linear change only in the initial phase. Since both cases have a

linear pattern, they were analyzed by the method of least squares and the range in which a straight line was considered statistically significant was clarified.

The correlation between the color difference or yellowing based on the exposure and the materials was assessed and the relation of each plastic in both exposure methods, which are the open air exposure and the sunshine fade-o-meter exposure, was also assessed. According to them, as for luster, when exposed to the open air, the correlation was recognized of PS, PMMA, and PE in color difference and of PS, PMMA, ABS in yellowing. In case of the sunshine fade-o-meter exposure, all plastics demonstrated a good correlation with color difference and yellowing. Although there were some difference of result between the exposure methods, the luster was found to have a close relation with color difference and yellowing due to the color change of the material.

3.2.4 Open Air Exposure and Accelerated Exposure

(1) Correspondence of the Open Air Exposure to the Accelerated Exposure in Dimensional Change

Based on the measurement results of chronological change of dimension in the various preservation circumstances and the dimensional and weight change due to the accelerated tests, the simple method to estimate the chronological change in dimension was evaluated using the repetitive

revolutionary expression. As a result, the effect of the accelerated test results, such as ultraviolet irradiation, and temperature cycle, corresponds well to the dimensional change in each preservation environment. It was confirmed that the estimation method of chronological change using the repetitive revolutionary expression was very useful.

The chronological change of the samples preserved in an ordinary room has a strong correlation with the dimensional change by the ultraviolet irradiation and the dry atmosphere. The dimensional change of the samples exposed to the open air is recognized to have a strong correlation with the dimensional change caused by the ultraviolet irradiation and the temperature cycle test.

(2) Regional Difference and Difference by the Accelerated Testers in the Weather Resistance

In the evaluation of the weather resistance of polymer materials, there is a variety in the degree and the pattern of degradation, in association with the degradation characteristics of the material tested, depending upon the environmental factors in the open air exposure test, and upon the optical distribution of the light source, the strength of the radiated optical energy, temperature, humidity, and watering conditions in the accele- /8 rated test. Therefore, development of the prediction technique to evaluate the weather resistance of the other accelerated testers or at the other districts, on the basis of the weathering test results of the particular

accelerated tester or at a particular exposure test location, is strongly needed. In order to do it, it is necessary to determine the quantitative correlations between the models, regional differences, and between the accelerated tester and the open air exposure. In this research, utilizing the 6 kinds of common samples, the changes of the property values and physical characteristic values obtained from the open air exposure in 4 locations, whose latitudes and environmental conditions are different, and also from the 7 accelerated testers in practice, were applied to the primary revolutionary, power, exponential and logarithmic curves. From the revolutionary expression which indicates a correlation factor (γ) 0.9 or higher, using the molecular weight and tensile strength of PS, PMMA, and so fourth as subjects, the numeration of the correlation between the models, regional differences, and between the accelerated tester and the open air exposure, was attempted.

Among those combinations, the expression $y = a + b \ln t$, or $\ln y = a + b \ln t$ is well applied between the exposure time (t) and the change rate (y). Therefore, the relation of the exposure time when the change rate (y) is equal can be written as $\ln t_i = A + B \ln t_j$, so that the equivalent time correlation between exposure methods can be expressed by a straight line on a bilogarithmic graph sheet.

As for the molecular weight changes of PS and PMMA, and the tensile strength changes of PS, POM, PE, and ABS, a considerable difference can be observed in the relation by various districts depending upon the materials

and the items measured. However, except for 2 or 3 specificities, the inclines (B) of the straight lines on the graphs are almost equal. As for the model differences observed in the molecular weight changes of PS and PMMA, the characteristics of each model have been quantitatively expressed.

3.2.5 Fading and Discoloration of Colored Plastics Caused by Open Air Exposure

As a part of research regarding weather resistance in the joint research, 5 resins and 6 dyes were selected and the colored plastic samples and plain materials for comparison were prepared. They underwent the open air exposure at 4 locations, i.e. Sapporo, Choshi, Yokohama, and Osaka, as the common colored samples. The measurement was repeatedly carried out in such a way that the colorimetry was performed to each level and then samples were exposed again. The effect of the various factors, such as kind of plastics, exposure time, and kind of coloring agents, to the fading and discoloration (UVW series color difference) of the exposed samples was evaluated. Also, the types of the discoloration speed curves and the possibility of quantization of the degree of fading and discoloration was assessed.

As for the fading and discoloration of the exposed colored plastics at 4 locations, the color differences were evaluated and the contribution of various factors, such as the kinds of materials and coloring agents,

exposure districts, and exposure time, were clarified. However, the contribution of exposure districts were not recognized as significant, except for some special cases.

In Yokohama, when the change of the color differences and the degree of yellowing of the materials after the exposure for up to 20 months was assessed in details, the degree of yellowing is highly affected by both the kind of materials and the exposure time. In two factors, the contribution of the former is greater.

When all the colored plastics were used as subjects, the coloring agents, the kind of plastics, and the exposure time show high significance to the color differences. However, as similar to the degree of yellowing, the contribution of the exposure time is small compared to other factors.

(1) Spectral Degradation

The spectral radiation experiment was performed to 6 kinds of the common sample films, polyethylene (high pressure method) (PE(H)), polyethylene (low pressure method) (PE(L)), polyethylene terephthalate (PETP), polycarbonate (PC), polyvinyl chloride (PVC), and polyamide (PA), and the wavelength dependency of the degradation was investigated. The evaluation of the degradation was done by the measurement of ultraviolet and infrared absorption spectrum, and dynamic elasticity. In PETP and PC, the wavelength dependency of the degradation almost corresponds to the original

ultraviolet absorption spectrum, and the wavelength of the maximum degradation certainly exists. In PE (H) and PE (L), the shorter the wavelength of the radiation, the more severe the degradation was supposed to be. However, an apparent maximum degradation wavelength is observed by the characteristics of the spectral distribution of the irradiated rays. PVC and PA also have a maximum degradation wavelength, but it is not clear whether it is unique to the sample or apparent like that of PE. It was commonly observed that the degradation got worse by the optical radiation of approximately 300-350 nm or lower rays.

3.3 Durability against the Thermal Conditions

3.3.1 Thermal Degradation

As for 8 kinds of the thermoplastic plastics, including the 6 common samples, and 5 kinds of the thermosetting plastics (compound materials), the thermal degradation phenomena in the air induced by the heat aging tester of forced heated air circulatory ventilation system were evaluated by the mechanical characteristics and the thermal degradation curves were obtained. Although there were some variations, the following characteristic phenomena were noted.

a) The materials selected for this research do not degrade for 10000 hours at the temperature of 100°C or lower.

b) The thermosetting plastics demonstrate improvement of characteristics due to the delayed hardening prior to the degradation at the

temperature of 150°C or higher (maximum 200°C).

3.3.2 Thermal Properties

As for the thermal properties of polymer materials, the tensile, bending, and shearing tests in both high and low temperature ranges were performed and the thermal dependency of the mechanical properties was studied. (Test temperature: -100°C - +130°C) As a result, in the low temperature range, the brittle phenomenon advanced and all the strengths including tensile strength increased comprehensively. In the high temperature range, each strength decreased as the temperature rose and each test became unmeasurable. Thus, they lost the strength as a material. However, the course during the tests of each sample material showed a different, unique fashion.

Regarding the mechanical properties in the low temperature range, in the tensile test, the brittleness progressed in the test piece and the tensile stress of each test piece generally increased lineally, shortening the /9 extension length until it fractured. Namely, it was found that the fracture energy decreased and the fracture stress increased. Moreover, adding the results of the bending and shearing tests, the various properties of plastics in the low temperature range was clarified. In the high temperature range, the tensile, bending and shearing strengths decreased as the temperature went up. Especially, PVC showed a rapid decrease at approximately 70°C. All the tests became unmeasurable and the sample lost the strength as a

material. In other samples, they could be measured until abrut 90°C-130°C.

Also, as a part of total evaluation, the correlation between the temporature property values and the fatigue property values was assessed. As a result, in the fatigue test, when the number of repetition is increased, the temperature goes up. This suggests that there is some correlation with the high temperature range.

3.3.3 Heat Properties

The glass transition temperature and melting temperature, which are the basic properties of polymer materials, were obtained by a differential scanning calorimeter (DSC) and the measurement of dynamic viscoelasticity. Also, the thermal conductivity, coefficient of linear expansion, and Bicat softening temperature, which are the practical heat properties of the materials, were obtained.

Since polymer materials change their physical properties, such as mechanical properties, dramatically at their glass transposition temperatures, it is very important to obtain them. Various glass transposition temperatures obtained precisely by DSC.

As for the thermal conductivity, which is a practical property, their temperature dependency was obtained. Since there are very few publicized data of the temperature dependency of thermal conductivity, there were

some unclear points, such as the relation with the glass transition temperatures. However, it was found that the thermal conductivity of PE decreased at the glass transposition temperature and became close to amorphous polymers. Regarding the coefficient of linear expansion, it was noted that there was a difference depending upon the directions because of the influence, such as the flow of resin during molding. Also, there was a correlation between the coefficient of linear expansion and the cohesive energy density of polymer molecules. The coefficient of linear expansion was found to be a constant dominated by the intermolecular force which prevent the rotation of molecules. As for the Bicat softening temperature, some resins have a high load dependency and other resins are not affected by the load.

3.4 Degradation due to the Chemical Circumstance

As polymer materials have been in use in many kinds of fields, the degradation of polymer materials in various chemical circumstances has become an important problem. When a polymer material is contacted to, or soaked in various chemical fluid, if the fluid is a real solvent, it takes a consequence from expansion to melting, of course. If the fluid is a non-solvent, the degradation occurs frequently although there is no change in appearance.

In the research, the degradation phenomenon of the solvents, which were supposed not to cause expansion and to have no altering effect to

polymer materials, was studied. In other words, 6 common samples were soaked in methanol, ethanol, water, salt water, and surfactant solution, for 5 levels of time period up to 10^6 minutes. Then, they were extended and destroyed by a tensile tester and the mechanical properties, such as strength, ductility, and elasticity, were measured. The fractured surfaces were observed by the scanning electron microscope.

As a result, the original samples of PVC, PS, and PMMA, which usually show the brittle destruction, are changed into ductility destruction by soaking in the fluid. Because those materials change from brittleness to ductility, the strength shows a minimum in the early phase of soaking and a maximum in the later phase, and then gradually decreases. The ductility decreases in the early phase of soaking, and later, rapidly increases and finally, gradually decreases. As for the kinds of solvent, in the early phase of soaking, ethanol has the most influence. In the later phase, methanol has the most influence. Among polymer materials, PMMA and ABS tend to be affected easily. POM and PE do not change their strength but show a large change in ductility. PVC is affected by water relatively considerably. Those phenomena can be explained as a complicated effect of various factors, such as solubility parameters of polymer and solvent, interfacial tension, entropy effect, and intermolecular force. However, a precise and clear confirmation, such as seen in dissolution phenomenon, can not be obtained. The destruction and the change in strength of polymers caused by temperature change can be considered identical to those caused by soaking in solvent in terms of the mechanism of destruction. It can be explained as a

result of simultaneous occurrence of two phenomena, i.e. the escaping of effective molecular chain due to the easiness in motion of the molecular chains, and becoming available due to loosening of coiled molecular chains.

3.5 Conclusion

Utilizing the six common samples as main subjects, and other additional samples of polymer materials, regarding the various outer conditions associated with durability, such as fatigue, creep, and abrasion as mechanical force, long term indoor preservation, open air exposure, and accelerated exposure as atmospheric condition, heat degradation and thermal properties as thermal condition, and soaking in solvent as chemical circumstance, the durability of polymer materials was analyzed and evaluated in terms of various mechanical properties, structural factors, morphological properties, and thermal properties, resulting in a vast collection of findings.

Those fruit include:

(1) As for the widely used standard 6 kinds of polymer materials (common samples), there is no other study like this research which measured and evaluated the wide variety of properties and characteristics systematically. This is a very useful information as the data which clarified the general properties of polymer materials as well as the durability systematically. This is also a very important data for the preparation of the optimum planning standards of polymer materials.

(2) In the course of the research, many problems regarding each test method, measuring method, and conditions of tester and measurement /10 were made clear. The part of those findings has been already used as the proposal to the establishment or revision of the Japan Industrial Standards. Many other data will be used as the fundamental data for the establishment of new standards or revision in future.

(3) The degradation mechanism and process of polymer materials under various degradation factors were made clear in terms of the structural factors, mechanical properties, and appearances. It supplied an important basic information for the molecular design of polymers with high durability, or for material design in the development of high durability polymer materials.

(4) As for the correlation between the wide variety of degradation factors and material properties associated with durability, the relation between degradation factors, district differences of open air exposure, model differences of accelerated exposure testing machines, specificity associated with materials and properties in terms of durability, were clarified. The useful data for comprehensive evaluation of durability was obtained.

(5) The change of durability against the mechanical forces, such as abrasion, fatigue, and creep due to open air exposure and indoor long term preservation was clarified. The basic data for the complicated evaluation

of durability, which simulates the practical conditions, was obtained.

Regarding the durability of polymer materials, this research supplied numerous useful information and will play an important role in the establishment of the comprehensive evaluation system of durability.

The author wishes that the fruit of this research consolidates the durability and reliability of polymer materials and contributes to the social needs, such as natural resource conservation, energy conservation, ensuring of safety, and consumer protection.

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APPENDIX-1 ORIGINAL DATA OF THE COMMON SAMPLES

Items		Units	Direction	PVC Average	PVC (S.D.)	PVC Dir.	PVC Total Average (S.D.)	PVDF Average	PVDF (S.D.)	PVDF Dir.	PVDF Total Average (S.D.)
Tensile	Yielding Strength	kgf/mm^2	L C	7.37 7.37	(0.05) (0.01)		7.37 (0.04)	- -	- -	-	-
	Fracture Strength	kgf/mm^2	L C	4.32 4.45	(0.06) (0.43)		4.39 (0.30)	8.32 8.47	(0.15) (0.05)		8.39 (0.13)
	Extension	mm	L C	54.30 11.30	(28.20) (5.40)	*	32.80 (29.70)	6.20 6.44	(0.57) (0.30)		6.32 (0.44)
Compression	Yielding Strength	kgf/mm^2	L C	8.10 8.36	(0.12) (0.20)	*	8.23 (0.21)	10.40 10.90	(0.20) (0.20)		10.70 (0.30)
Bending	Bending Strength	kgf/mm^2	L C	10.20 10.00	(0.90) (0.30)		10.10 (0.70)	8.72 9.16	(0.26) (0.11)	**	8.94 (0.20)
	Bending Coefficient of Elasticity	kgf/mm^2	L C	345 345	(4.00) (3.90)		345 (3.80)	330 316	(6.50) (15.70)		325 (13.40)
Impact	Charpy Impact Value (#1)	$kgf/cm/cm^2$	L C	4.03 3.69	(0.65) (0.46)	**	3.86 (0.56)	2.30	(0.06)		
	Charpy Impact Value (#2)	$kgf/cm/cm^2$	L C	2.56 2.05	(0.07) (0.08)		2.30 (0.28)	1.62	(0.06)		
	Izod Impact Value	$kgf/cm/cm^2$	L C	2.52 2.50	(0.12) (0.14)		2.51 (0.12)	2.15	(0.05)		
Plcat Softening Point	Load 1kg 2kg 3kg 4kg	°C		103 86 82 79				116 112 110 108			
Linear Expansion Coefficient	Temp. Rising Speed 1°C/min	10^{-5}cm/cm/°C	L C	5.87				6.00			
	Temp. Rising Speed 10°C/min	10^{-5}cm/cm/°C	L C	4.55				5.25			
Abrasion	ASTM-A type TABER type	mg mg		286±60 136±18				443±25 457±45			
Hardness	Barcol 934-1 Barcol 935			25±1 84±1				50±0 92±1			
	Rockwell M Rockwell R			77(2.6) 125(0.7)				101(1.4) 125(0.6)			
Fatigue	Biplene Vibration One Side Tensile	kgf/mm^2		0.8-1.3 0.9				2.0-3.0 1.4			

APPENDIX-2 ORIGINAL DATA OF THE COMMON SAMPLES

POM				ABS				PS			
Average	(S.D.)	Dir.	Total Average (S.D.)	Average	(S.D.)	Dir.	Total Average (S.D.)	Average	(S.D.)	Dir.	Total Average (S.D.)
6.66 6.46	(0.03) (0.02)	**	6.65 (0.11)	4.45 4.42	(0.02) (0.02)		4.42 (0.02)	- -	- -	-	- -
5.85 5.56	(0.20) (0.18)	*	5.71 (0.24)	3.64 3.44	(0.07) (0.02)	*	3.49 (0.07)	4.14 3.98	(0.14) (0.23)		4.06 (0.20)
24.80 42.20	(5.10) (9.30)	**	33.50 (11.60)	9.73 15.90	(2.12) (5.30)	*	12.80 (5.0)	1.84 1.64	(0.06) (0.27)		1.74 (0.21)
8.61 7.79	(0.17) (0.15)	**	8.20 (0.45)	5.54 5.49	(0.03) (0.03)	*	6.52 (0.04)	10.20 10.30	(0.10) (0.10)		10.20 (0.10)
8.23 8.03	(0.12) (0.16)		8.13 (0.07)	6.51 6.46	(0.04) (0.06)		6.49 (0.05)	6.00 5.66	(0.27) (0.22)		5.83 (0.30)
308 297	(9.40) (3.30)		3.03 (8.70)	210 207	(1.00) (2.50)		208 (2.4)	315 339	(7.20) (7.10)	**	327 (14.4)
10.13 9.69	(0.66) (0.96)		9.91 (0.81)	23.36	(0.82)			1.62 1.46	(0.20) (0.09)		4.54 (0.17)
6.26 6.33	(0.34) (0.23)		6.30 (0.28)	24.36	(0.18)			1.22 1.17	(0.14) (0.16)		1.19 (0.15)
6.09 5.45	(0.19) (0.34)	**	5.77 (0.42)	31.07	(1.02)			1.07 1.17	(0.13) (0.08)	*	1.09 (0.13)
161 159 156 153				98 95 92 90				93 92 91 90			
9.66				9.10				6.92			
7.42				7.32				6.11			
199±76 114±14				743±65 456±49				585±52 160±59			
- 73±1				- 64±1				25±1 81±1			
84(1.8) 121(0.7)				- 106(0.5)				82(1.6) 125(0.7)			
3.0-3.4 1.8				0.5-1.6 0.8				0.4-0.8 0.4			

APPENDIX-3 ORIGINAL DATA OF THE COMMON SAMPLES

PE				Testing Method	Remarks
Average	(S.D.)	Dir.	Total Average (S.D.)		
3.07 3.09	(0.02) (0.07)		3.08 (0.05)	Follow JIS K 7113	L: flow direction C: vertical direction Direction (Dir.) ** Significant at 99% * Significant at 95% No symbol No significance
2.67 3.03	(0.57) (0.51)		2.85 (0.54)		
329 445	(67) (50)	*	387 (83)		
2.48 2.75	(0.79) (0.10)		2.61 (0.55)	Follow JIS K 7208	
2.46 2.78	(0.04) (0.02)	*	2.62 (0.17)	Follow JIS K 7203	
160 178	(5.60) (5.50)	*	169 (10.6)		
40.07 30.85	(1.12) (1.23)	**	35.77 (5.33)	JIS K 7111	
25.70 18.85	(1.07) (0.30)	**	22.28 (3.67)		
51.01 35.93	(1.17) (1.03)		42.63 (8.01)	JIS K 7110	
126 117 100 92				ASTM D 1525	Test Piece 3x20x20 mm
12.74					At about -40°C, temperature is increased at a constant rate and measured. Coefficient of expansion between -30°C and +30°C. Test Piece 3x10x40 mm
9.55					
66±100 23±5				JIS K 7205 JIS K 7204	Measured at 20±2°C, 65±% Values are average and 95% reliability limit.
- 29±1				Follow ASTM D 2583	
- 58 (3.1)				Follow JIS K 7202	Values are average and the bound ( )
1.2-1.3 0.8				Follow JIS K 7119	Stress amplitude Total amplitude

APPENDIX-4 ORIGINAL DATA OF THE COMMON SAMPLES

			PVC	PMMA
Heat Conductivity	-50°C -30 0 20 40	10^{-4} cal/ cm^2 °Csec	3.6 3.7 3.2 3.7 3.7	4.4 4.5 5.4 4.6 4.5
Transposition Temperature	DSC	°C	44 78	123 122
	Dynamic Viscoelasticity E" Peak Temperature	°C	78	46 115
Optic Properties	X Y Z		0.832 Ⓣ 0.852 0.973	0.912 Ⓣ 0.930 1.096
Creep	100 Hr Creep Strength Creep Elasticity**	kgf/mm^2	4.28 352	4.92 245
Molecular Weight and Molecular Weight Distribution	Mn Mw Mw/Mn Mn Mw [η]	$\times 10^4$ $\times 10^4$ $\times 10^4$ $\times 10^4$ dl/g	3.32±0.06 8.00±0.06 2.42±0.05 4.0 8.5 0.848	87±3.1 221±2 2.44±0.09 96 195 4.21
Density	$10^3 kg/m^3$		1.3920	1.189
Method of Sample Preperation			PVC Geon 103EP-8 100 Orgranic tin malate series TS 201 M 1.0 TS 208 M 1.0 Tin Laurate Series TS1013 0.3 Tin Mercaptane Series #2399 1.0 Ultraviolet inhibitor: Tynupine 0.05 Lubricant Calcoat 86 0.5 Hiblen 1.0 Gelling agent trace Manufacturing Condition Mixture, Kneading, Preheating, Calender, Press Molding	Acrylite S No. 001 (clear) 3mm (only Catalog) Methacrylic resin molding plate

APPENDIX-5 ORIGINAL DATA OF THE COMMON SAMPLES

POM	ABS	PS
- - - - -	4.4 4.0 4.6 4.2 3.6	4.3 5.1 4.9 3.7 3.7
167**	65 108 130	97
105**	103	96
0.544 0.558 Ⓡ 0.609	0.433 0.442 Ⓡ 0.360	0.876 0.894 Ⓣ 1.053
4.50* 268	3.13 170	2.37 463
- - - - - -	- - - - - -	14.1±0.3 43.6±0.4 3.09±0.06 16.6 40.0 1.177
1.413 s	1.043 o	1.047 o
Duracon (Composition Patent Bulletin No. 36-14640) Base Monomer: Trioxane Comonomer: Environmental Ether Molding (sheet) Injection Condition: Grade M25 Dise Used: Coat Hanger Dise Cylinder Temperature C1 (Hopper side): 170°C C2: 175°C C3: 190°C C4 (Tip side): 185°C Dise: 185°C Roll temperature: 120°C Screw Rotation Speed: 40-60 rpm Injection Pressure (Adapter side) 50-80 kg/cm2	Cycolac GS-E (only in Catalog)	Denka Styrol MW-1-301 (only in Catalog) Molding, Ikegai Tekkojo, Plastic Technical Center Molder: Ikegai ES 90-28 Bent Injector + DS 1000 Sheet Molding Machine Molding Condition Screw die cylinder temperatuer 185°C Die entrance temperature 233°C (Die tip temperature 196°C) Sheet molding machine Polishing roll temperature (upper roll 76°C) (middle roll 71°C) (lower roll 93°C)

APPENDIX-6 ORIGINAL DATA OF THE COMMON SAMPLES

PE		
18.7 14.3 12.6 9.7 9.9	Unstationay thermal flow method	Sample: laminated layers of 3 mm 2 plates of 150x150x50
134*	DSC-type 2	Temperature rising speed 10°C/min, * Melting point
70**		Frequency measured: 10Hz Temperature rising speed: 1°C/min ** Crystal dispersion temperature
0.505 0.519 (R) 0.662	JIS Z 8722	(T) Transperent Measurement (R) Reflex Measurement (Black background)
1.07* 118	Follow JIS K 7115	* 10% strain strength ** Low stress range 10^{-2} hours
1.28±0.03 22.0±0.5 17.3±0.7		GPC } PVC, PMMA GPC } PS THF 40°C GPC } PE O-dicyclobenzene 135°C Osmotic pressure Optic dispersion THF, 35°C
0.959 0	JIS K 7112	Accuracy ±0.7 kg/m^3 (measured at 20°C) (reliability 95%)
Mitsui Petroleum Chemistry, Co.	(underwater transposition method)	